KINGDOM OF BELGIUM 704 297

No. 704 297 [Belgian Coat of Arms] [illegible stamp]

MINISTRY OF ECONOMIC AFFAIRS

IMPROVEMENT PATENT

The Ministry of Economic Affairs

Pursuant to the law of 24 May 1854 on patents, and especially its Art. 14 and 15;

Pursuant to the report drawn up on 26 September 1967 at 14 h 50 *at the* Industrial Property Department;

DECREE:

Article 1: - *There is granted to* the company known as: CONTINENTAL OIL COMPANY, 1000 South Pine Street, Ponca City, State of Oklahoma (United States of America),
represented by Mr P.Hanssens in Brussels,

an improvement patent for: Process and apparatus for coating sheets of solid materials, patented in its favor on 10 March 1965 under No. 660 885, which improvement it declares to have formed the object of an addition patent filed in France on

20 April 1966 and granted on 11 September 1967 under No. 90 125.

The invention has also formed the object of a patent application, not yet granted to date, filed in the United States of America on 13 September 1965, No. 486 787.

Article 2. *This patent is granted to it without preliminary examination, at its risks and perils, without guarantee either of the reality, of the novelty or of the merit of the invention or of the accuracy of the description and without prejudice to the rights of third parties.*

To the present decree will remain appended one of the copies of the specification of the invention (description and possibly drawings) signed by the concerned party and filed in support of its patent application.

Brussels, 31 October 1967

BY SPECIAL AUTHORITY

The Chief Executive Officer,

[illegible signature]

No. 0740

0741

0742

CS

US. 486 787

FIRST IMPORTATION IMPROVEMENT PATENT

"Process and apparatus for coating sheets of solid materials"

Company known as : CONTINENTAL OIL COMPANY

Main importation patent filed in Belgium on : 10 March 1965 and granted under No. 660 885

FIRST IMPORTATION IMPROVEMENT PATENT based on the first French certificate of addition No. 90.125 filed on 20 April 1966 and granted on 11 September 1967 on behalf of the APPLICANT COMPANY. A corresponding application was filed in the United States of America on 13 September 1965 under No. 486 787.

The present invention relates to a process and an apparatus for applying a coating in the form of a membrane to at least one surface of a substrate. Within narrower limits, the present invention relates to a

process and an apparatus for improving the dimensional uniformity, appearance and continuity of thin coatings of hot materials in the molten state when these materials are applied in the liquid form to sheets of substrate-forming solid material. Mention may be made, as examples of these substrate-forming materials, of milk cartons, boxes for frozen foods, various kraft, sulfite and crystal papers, paper and metal foil laminates, sheets of synthetic resin and plywood.

When they are applied to the coating of certain solid materials used as substrate with hot viscous liquids, such as a molten wax, molten synthetic resins and mixtures of waxes with synthetic resins (generally known as hot molten masses), most of the coating processes currently used are characterized to varying extents by a number of disadvantages. Mention may be made, among these disadvantages, of a loss or a not very economical use of the coating material, a decrease in the flexibility of the substrate following the coating and the unsuitability of the coating technique for successfully applying a continuous and smooth coating which is devoid of crazing, pitting and blistering.

Several of these disadvantages have been particularly characteristic of the so-called "curtain coating" process, in which the material is passed through a falling film or curtain of the coating medium, so that the latter reaches the exposed surface

of the material and is deposited thereon in the form of a thin and relatively uniform film. The excess coating material which does not deposit on the material is collected in a suitable receiving container and is recycled to the starting point of the descending curtain in order to be reused. In many cases, after having coated the substrate, it is cooled by immersion in cold water or by another appropriate means, in order to harden the coating and to confer a glossy appearance on it, and is subsequently dried.

In the main patent, the Applicant Company disclosed a process and an apparatus which can be used to improve the coating formed on a solid substrate on applying a hot molten composition to the substrate. The improvement obtained lies mainly in the decrease in the amount of the coating composition necessary to obtain the desired defect-free uniform coating and in the removal of the defects, such as holes, bubbles or blisters, from the coating. The process disclosed in the main patent is applicable in particular to coatings applied by the curtain coating process and generally comprises an initial heating of the material of the substrate to be coated to a temperature sufficient to allow a uniform and smooth layer of the desired coating composition to be deposited on the material and then the application of the liquid coating composition in a state devoid of gas to at least one side of the material.

The Applicant Company has now surprisingly discovered that, in contrast to its previous assumption, it is pointless to heat beforehand numerous types of solid substrate before applying thereto the preferred viscous coating compositions, comprising a wax and a synthetic resin, in order to obtain satisfactory coatings relatively devoid of defects. Although a preliminary heating of the substrate is still an advantageous and generally desirable stage of the process in the case of most types of materials forming the substrates, the Applicant Company has found that, in the case of numerous types of materials, the coating obtained is nearly as good without a prior heating stage as when the substrate is initially prepared by a preliminary heating, as disclosed in the main patent.

In the case of a few heat-sensitive substrate materials, very little or no prior heating may be accepted. In contrast, according to the experience of the Applicant Company, dense and relatively nonporous materials, such as a cylinder board forming a milk carton and analogous materials, require a prior heating in order to allow a uniform and defect-free coating to be deposited thereon.

The fact of being able to dispense with the preheating stage of the process disclosed in the main patent in many cases without however producing a coating of lower or unacceptable quality, as has been

determined by the Applicant Company, makes it possible to achieve an important aim of the invention, that is to say an additional decrease in the cost of the application of a smooth, uniform and defect-free coating to various types of substrates.

In addition, the present invention intends:

- to generally improve the coatings which can be applied to various substrate materials when the latter pass through a falling curtain of the coating composition;

- to provide a process and an apparatus for applying a smooth and uniform film of a viscous coating composition comprising a wax strengthened by a thermoplastic resin to one or other side or to both sides of a sheet of fibrous material;

- to improve the appearance of the coatings comprising a wax and a resin on flat fibrous materials by improving the dimensional uniformity and continuity of these coatings;

- to improve the flexibility of a fibrous material which has been coated with a hot coating composition comprising a wax or a copolymer of a wax and which has been subjected to a drying medium during the subsequent hardening of the coating;

- to improve the rate at which a flat paper can be coated with coating compositions having a highly varied viscosity and highly varied chemical compositions;

- to improve the continuous adhesion of the coating compositions to fibrous materials to which they are applied.

The aims shown, and others of the present invention, are achieved by using a coating process which generally consists in removing substantially all entrained and undissolved air or other gas from a composition in the form of a hot molten mass which has to be applied to a solid substrate in the form of a thin coating and in then applying the composition in the form of a hot molten mass in the state substantially devoid of gas to one side of the material. The coating is applied to the substrate in the form of a thin film deposited substantially parallel to the surface to be coated and substantially in continuous contact with it. In the case of the majority of the materials, the material is preferably heated beforehand before the application of the composition in the form of a hot molten mass substantially devoid of gas but, with numerous types of materials, a satisfactory coating can be obtained for virtually any application without such a prior heating. For reasons which are not fully understood, if such a prior heating is not carried out, it is difficult in the case of numerous thick papers to apply uniform coatings to both sides of this material using mixtures of an oil-derived paraffin or wax and of synthetic resinous copolymers.

The preferred preheating treatment of the various substrates varies with regard to its usefulness and with regard to the degree to which it improves the coatings applied to the materials. In the case of some materials, it is desirable not only to heat the material beforehand before the application of a first coating but it is also highly desirable to heat the material beforehand before the deposition of the second coating on the opposite side of the material with respect to that which exhibits the first coating. With materials of this type, the second heating makes it possible to obtain a much better adhesion and a more uniform thickness of the coating which is applied to the second side of the material. In the case of other types of materials, in particular relatively thick materials, a single prior heating before the application of the first coating is sufficient if the second coating is applied immediately after the application of the first coating.

The degassing of the coating composition before its application to a substrate is regarded as being an important feature of the invention, given that the imprisoned gas significantly reduces the thickness of the coating at the location of the gas bubbles and results in the formation of holes in the coating. An important condition of most of the coatings is the protection of the substrate material or of the packaged products which are wrapped in the coated product. In

many cases, the protective coating has to constitute an effective barrier to the transfer of gases. When bubbles are found in the coating, they reduce its thickness and the properties of a barrier preventing the passage of vapor of a coating are a direct function of the thickness of the coating. Consequently, the entrainment of a gas which is reflected by the formation of bubbles, of hollows or of holes is harmful to the properties of a barrier preventing the passage of vapor of the coating. The entrainment of gas is a significant problem in particular when very viscous coating compositions are used, such as mixtures of a paraffin and/or microcrystalline wax with compatible synthetic resins. Substantially all the undissolved entrained gas is removed from the coating composition by the vacuum centrifugal rectification process preferably used in the present invention and described hereinbelow. The Applicant Company has found that much thinner coatings with fewer defects of very viscous compositions can be deposited by using this process than those which can be obtained when a less efficient or no degassing of the composition is carried out before applying it to the substrate. Thus, the efficient degassing according to the present invention makes it possible to achieve a significant saving in the costs of material because of the thinner coatings which can be obtained in a satisfactory fashion. In addition, when very viscous coating compositions have

to be applied at appreciably low temperatures, because of the heat-sensitive nature of the substrate, the degassing as carried out in the present invention makes it possible to use these viscous compositions for certain coating applications in which it was not possible to use them hitherto.

With numerous types of fibrous materials, a preheating of the materials has the disadvantage of reducing the flexibility of the material as a result of dehydration or a significant decrease in its moisture content. Even without having recourse to preheating, the fact of bringing the material into contact with the hot coating composition has a tendency to remove moisture from the material. Thus, in general, the higher the temperature to which the material is heated beforehand, the more significant the problem posed by the decrease in the moisture and the more pronounced the decrease in the flexibility of the material. In any case in which the flexibility of the coated material constitutes a significant characteristic, it is consequently preferable to dispense with the prior heating, if it is possible to obtain satisfactory coatings without such a preheating. On the other hand, when a preheating is highly desirable or necessary, the present invention envisages humidifying the atmosphere in which the material is initially preheated, in order to prevent a subsequent decrease in the moisture content and a reduction in the flexibility.

The apparatus with which an embodiment of the present invention is implemented comprises a curtain-coating device which can be of a conventional type and which operates to provide a film or a curtain delivered downward or falling film or curtain of the coating composition; a conveyor or a means for moving the material through the falling curtain of the coating composition; a pipe for collecting and recycling to the curtain-coating device the excess coating composition which is not deposited on the material to be coated, and any extra coating composition or coating composition added afterward which can be added to the plant; and a means used in combination with the pipe for removing the undissolved and entrained gases from the coating composition during its recycling to the curtain-coating device. An important feature of a preferred embodiment of the apparatus used for the implementation of the invention is the specific type of apparatus or of device which is preferably used to remove or extract the undissolved entrained gases from the coating composition. The degassing apparatus comprises a means for spreading the coating composition in the form of a thin film while agitating it and a means for applying, to the agitated thin film, a pressure of less than atmospheric pressure or a vacuum, so as to remove any undissolved entrained gas which may be present in the composition.

It is also desirable to incorporate, in the apparatus used for the implementation of the invention, a humidifying means for adding a sufficient amount of moisture to the material to be coated in order to prevent excessive dehydration of the material and to avoid the fibers being rendered brittle in the case where the material is preheated before the application of the coating. Another advantageous component which is preferably provided in the apparatus is an additional heating means for reheating or further heating the material before the application of the coating composition to its second side. The plant also comprises the usual and conventional additional equipment which is used in combination with existing curtain-coating machines for maturing the coatings applied to the material, such as a water bath, a waterfall, cold air or a cold surface, in order to cool the coated material, and an appropriate device for removing the excess water from these surfaces in the case where the coated material is brought into contact with water for cooling purposes. Other advantages and characteristics of the invention will emerge from the description which will follow given with regard to the appended drawing, in which:

Figure 1 is a flow diagram which shows the path of the material to be coated through the apparatus used for the implementation of the invention and the path

for the flow of the coating composition which is used for the implementation of the invention;

Figure 2 is a rather diagrammatic cross section of a degassing apparatus of a preferred type used in the implementation of the process of the invention.

At the beginning of the process of the invention, the material to be coated can usually be optionally subjected to a preheating by an appropriate heating device 10. The latter can be an oven at a constant temperature with a forced air stream which is sufficiently large to comprise materials of any size which it may be desired to coat, but it is not limited to such an oven. Heated rollers or infrared radiation heating elements can also be used. The period of time during which the material is preferably heated and the temperature to which it is heated depend on the type or on the composition of the material to be coated, on the specific coating composition which has to be applied thereto and, to a certain extent, on the thickness of the material.

In the case of a coating of substrates which are made of fibrous material, such as "kraft", sulfite and crystal paper, boards, and the like, the preheating technique, when it is used, with the application of the hot coating composition and the subsequent drying of the coated material, all have a tendency to greatly reduce the moisture content of the fibrous material, resulting in a decrease in its flexibility and

rendering it rather brittle. Consequently, it is desirable only to heat the material beforehand when this is necessary in order to obtain a finished coating having the desired quality and the desired thinness. It proved to be the case that generally the flexibility of the material is affected in a more harmful way by high temperatures than by an increase in the duration of the heating period. To avoid these losses in moisture, the present invention provides for the provision, jointly with the heating device 10 provided for initially preheating the material, of an appropriate humidifying device 12 which, in its simplest form, can consist simply of a water container which is placed in an oven. During the heating of the material, the moisture or the water vapor provided by the humidifying device 12 has a tendency to compensate for the amount of moisture from the material which would otherwise be lost by the simultaneous or subsequent heating.

From the heating device 10, the material is transported by the conveyor 14, which is represented diagrammatically in the drawing, under a row of infrared radiation heating elements 15 to a curtain-coating device of a conventional type, such as a Steinemann curtain coater, represented by the reference number 16. The row of the infrared radiation heating elements 15 is positioned in an appropriate way above the conveyor 14 and can be used for an additional or

complementary heating of certain types of materials in the way described below.

The curtain-coating device 16, as described above, provides a descending curtain of the coating composition which moves in a vertical plane substantially perpendicular to the plane in which the material to be coated moves. The curtain of coating material usually has a greater width in the transverse direction than the material which has to pass through it, so that a portion of the coating composition passes wide of the material and falls into a collecting container or a receiver (not represented). In a preferred embodiment of the invention, the excess coating composition which is collected in the receiving container flows by gravity into an intermediate tank 17. The level of the liquid of the coating composition present in the intermediate tank 17 can be adjusted by an appropriate device for regulating the level of the liquid, which can comprise a control valve 18. The control valve 18 is positioned in a pipe 19 which is used to transport the coating composition from the intermediate tank to a degassing device 20.

The degassing device 20 can be any appropriate type of apparatus for degassing a liquid but it is preferably a vacuum centrifuge unit such as that sold under the registered tradename "Versator" by Cornell Machine Company Inc. of Springfield, New Jersey. The construction and the operation of the "Versator" vacuum

centrifuge device are well known to experts but it has been represented in a fairly diagrammatic fashion in Figure 2, in order to make possible a better understanding of the way in which the degassing is preferably carried out in the implementation of the present invention.

The degassing device 20 as represented in Figure 2 comprises a figured tank or chamber 21 which is connected via a pipe 22 to a vacuum unit 23. The vacuum unit 23 thus applies a vacuum to the chamber 21 in order to reduce the pressure therein well below atmospheric pressure. The pipe 19 enters the chamber 21 and comes to an end at the center of this chamber in the form of a flared diffusing ring or disk 24 which distributes the coating composition over a large area below the diffusing ring. A controlled rotary shaft 25 enters the chamber 21 and extends through an appropriate bearing situated in the wall of the chamber 21 and carries, at its end situated inside the chamber, a centrifuge bowl 26. The latter has a bottom with a concave shape which is curved back over itself along its peripherally external edges to form a lid and a bottom for the bowl which are integral. As the hot coating composition is being spread towards the outside from the diffusing ring 24, it is deposited on the bottom of the centrifuge bowl 26 which is rotated at high speed by the shaft 25. The coating composition is thus spread in the form of an agitated thin film which

is subjected to the vacuum generated in the tank 21. As the composition is being displaced towards the outside on the centrifuge bowl 26 by the centrifugal force, it accumulates in the angle formed by the folded back part forming the lid of the centrifuge bowl. The accumulation of the coating composition at this angle makes it possible to remove it from the degassing device 20 under the action of the centrifugal force.

Thus, by passing a pipe 27 through the wall of the chamber 21 and into the angle of the external periphery of the centrifuge bowl 26, the accumulated coating composition is discharged under the influence of the centrifugal force into the main tank 28 reserved for the hot molten mass. It is simply a heated tank for the coating composition, which is used to maintain the composition at the desired temperature before recycling it to the curtain-coating devices. The hot coating composition is supplied from the tank 28 to the coating devices by means of pumps 29.

Since it is very often desirable to coat the second side of the sheet of fibrous material with the coating composition, as well as its first side, a second curtain-coating device 30 can be provided and it can be connected to the first coating device 16 by means of a conveyor 32. In some cases, it is desirable to provide additional heating of the material after the first coating has been applied to it and before the application of the second coating. For this purpose, a

second row of infrared radiation heating elements 31 is inserted between the first curtain-coating device 16 and the second curtain-coating device 30. An appropriate oven can also be used to provide the necessary additional heating. Given that it is obviously necessary to turn over the material on the conveyor 32 before it passes under the second row 34 of infrared radiation heating elements and before it enters the second curtain-coating device 30, an appropriate means (not represented) is provided for turning over the material or for bringing about this reversal. Although it is possible to carry it out manually, an appropriate mechanical means of any type can be used for carrying out the reversal of the material.

In the second curtain-coating device 30, the material again passes through a falling film or curtain of the coating composition and receives, on its second side, a uniform thin layer or coating of a gas-free coating material. From the second curtain-coating device 30, the material, which is now coated on both sides, can pass through a cooling device 36 in order to cool the material and in order to fix or harden the coating composition. If the cooling device is a water bath, the material passes through an appropriate drying device 38.

The stages used in the process of the present invention have been described generally, given that it

is not possible to set precise limits with regard to the extent to which the materials can be heated beforehand and with regard to the amount of moisture which is advantageously supplied to the material by the use of the humidifying device 12, when a preheating is used in the process of the invention. A number of variables have to be taken into account in determining the best preheating temperature to be used in any given case and these variables determine whether heating has or has not to be used in the case of each material. For example, the affinity of a specific material for the coating composition which has to be used, the geometric dimensions of the material to be coated, the viscosity and the chemical composition of the coating which can be used, the porosity and the density of the material or substrate used and the final application which is envisaged for the coated material constitute variables which have to be taken into account in determining whether preheating of the material is or is not necessary and, if preheating is carried out, the temperature at which the preheating is carried out. It may be generally established, when preheating is used for the purpose of preventing the accumulation of gases in the sheet of substrate or on its surface, so as to prevent the formation of bubbles, holes and blisters in the coating, that the degree of preheating is such that these gases either expand to a greater extent than when the coating in the form of a hot molten mass is applied

or at least to an extent such that, if an additional expansion of the entrained gas takes place, this expansion does not burst or does not otherwise significantly affect the characteristics of uniformity of the coating.

When preheating is used to improve the bonding between the substrate and the coating, the degree of preheating is such that the warmth of the surface of the material to be coated is sufficient to compel the coating to remain [illegible] for a longer time and thus to promote faster and stronger anchoring of the substrate to an extent necessary to satisfy the conditions of the final application envisaged for the coated material.

In some cases, it is desirable to heat the material beforehand, before depositing the coating composition on each of its sides, to a temperature which is close to or even exceeds the temperature of the hot coating composition to be applied thereto. In the case of numerous types of thicker fibrous materials, these materials can frequently be provided with uniform and smooth coatings without it being necessary to heat the coating beforehand between the application of a coating to its first side and the application of the coating composition to its opposite side. It seems that, in the case of thinner or less bulky materials, the heat from any heating of the material which is carried out before the application of

the first coating can be more easily lost by radiation and conduction than in the case of thicker and bulkier materials, so that, as a general rule, an additional heating during the intermediate period between the application of the first and second coatings is more desirable in the case of thinner materials than in the case of bulky or thicker materials.

In the case of some materials, the use of an oven at constant temperature, in conjunction with heating by infrared rays, gives the best form of preheating of the material. In this case, which usually relates to thinner or less bulky materials, it seems that the heating by means only of an oven does not supply the necessary heat to the surface of the material, so that good adhesion and good continuity in the coatings applied to the material are not obtained.

The application of the present invention in providing better coatings on various types of substrate-forming materials is illustrated in the following examples. Although it is possible to use other compositions in the form of hot molten masses, the coating composition used is a mixture of a paraffin wax and/or of a microcrystalline wax with a copolymer of ethylene and of vinyl acetate. The copolymer generally comprises from 10 to 40% by weight of vinyl acetate and it can be conveniently prepared by copolymerizing a mixture of ethylene and of vinyl acetate in the presence of a catalyst which generates

free radicals, for example tert-butyl hydroperoxide, in an appropriate reactor under a pressure of between 1 050 and 2 100 kg/cm^2 and at a temperature of between 150 and 250°C approximately. The melt index of the copolymers of ethylene and of vinyl acetate which are of use in the mixtures of paraffin waxes used to coat certain substrate-forming fibrous materials is between 1 and 500 approximately, preferably between 3 and 300 approximately. These melt indices are determined by the ASTM D-1238-57T test method and are expressed in grams of the copolymer which can be pushed through a normal orifice in 10 minutes at 190°C by means of a piston weighing 2 160 grams. Compositions formed of copolymers of ethylene and of vinyl acetate and of wax which can be used in the implementation of the present invention are typically those which comprise from 80 to 30 parts of wax and correspondingly from 20 to 70 parts approximately of the copolymer.

Generally, any composition can be used in the form of a hot molten mass in the implementation of the invention provided that, when a curtain-coating machine is used to form a falling curtain, the fluid flow characteristics of the composition allow it to be pumped through the coating head at a flow rate sufficient to maintain the curtain. It must be emphasized that the degassing stage of the process is highly efficient and is of the utmost importance for the application of good coatings in the case of coating

compositions in the form of a hot molten mass which exhibits a viscosity of at least 300 cPs at temperatures of at least 149°C. Certain compositions cannot be used for curtain coating processes unless a rigorous degassing of the type disclosed by the present invention is carried out.

It is clearly understood that the expression "composition in the form of a hot mass" used in the present application is defined in the commonly accepted way as comprising a mixture of oil-derived waxes with modifying agents which are compatible with the wax, in which mixture the percentage by weight of the modifying agent present is greater than 10%. Other examples of compositions in the form of hot masses are mixtures of microcrystalline wax and/or paraffin wax with copolymers of ethylene and of ethyl acrylate, with copolymers of ethylene and of isobutyl acrylate, with polyethylene, with polyisobutylene, with ethylcellulose and with copolymers of butadiene and of styrene.

The following examples are given by way of illustration but without implied limitation of the invention.

Example 1

A material for a milk carton with a capacity of 1.89 liters which is cut out from a cylinder board and which has a thickness of 0.55 mm constitutes the material used. The coating composition used is a mixture of a wax and of a copolymer comprising:

30% by weight of a copolymer of ethylene and of vinyl acetate comprising from 30 to 35% by weight of vinyl acetate and exhibiting a melt index of between 20 and 30 approximately,

35% by weight of paraffin wax (melting point from 52 to 54°C),

30% by weight of microcrystalline wax,

5% by weight of low molecular weight polyethylene,

25 parts per million of an oxidation inhibitor.

The material or board is placed in an oven maintained at a constant temperature of 177°C for two minutes before the coating of the first side in a Steinemann curtain-coating apparatus. After the residence time indicated in the oven at constant temperature, the material is moved through the curtain-coating device on an appropriate conveyor and the first side is coated with the indicated coating composition, degassed in the way described above. The material is subsequently coated on its second side or opposite side without applying additional heat before the second coating. The material is subsequently cooled by immersing it in cold water. The material exhibits continuous coatings devoid of holes on both sides with a glossy and pleasing coating on the second side.

During another test, in which the prior heating of the milk carton is omitted, a coating of the first side is obtained which is of acceptable quality.

However, when the coating composition is applied to the second side, coatings are obtained which are full of holes, of hollows and of other defects. These defects render the boards or cartons unusable as liquid containers.

Example 2

Use is made of a board for a milk carton with a capacity of 0.95 liter from a cylinder board. This material has a thickness of 0.4625 mm. The coating composition is the same mixture of wax and of copolymer as that used in Example 1. The material is placed in an oven maintained at a constant temperature of 216°C for 45 seconds. After exiting from the oven, the material passes under a row of infrared radiation heating elements positioned at 10 cm above the material, which gives a residence time under the row of approximately half a second. The coating composition is then applied to the first side of the material.

After the coating of the first side of the material, the material is again passed under a row of infrared radiation heating elements positioned 10 cm above the second uncoated surface of the material, with a residence time under the row of approximately half a second. The second side of the material is then coated and the material is cooled by immersing it in cold water. The coatings on both sides of the material are continuous and devoid of holes. A pleasing and glossy coating is obtained on the second side of the material.

In both Examples 1 and 2, a vacuum centrifuge unit of the "Versator" type described above was used to remove the entrained gas from the coating composition. The vacuum generated in the degassing unit is generally sufficient to suck the coating material into the device and the centrifugal force created in the device is sufficient to discharge the degassed material into the tank 28 reserved for the hot molten mass represented in the drawing. The unit was used with success to degas mixtures of a paraffin wax and of a microcrystalline wax with the copolymer described above.

Although the coatings which were deposited on both sides of the material, as described in Examples 1 and 2, are very uniform and devoid of defects, the final material exhibits a certain decrease in its flexibility due to a decrease in its moisture content as a result of the preheating. In order to compensate for the decrease in the moisture content, additional tests are carried out during which the atmosphere present in the oven maintained at a constant temperature used for preheating the material is humidified and the prior heating is carried out at a temperature below that used when humidification is not provided. Examples 3 and 4 illustrate the implementation of the process of the present invention in which the material is subjected to a humid atmosphere during the preheating stage.

Example 3

The material used in this test is a board for a milk carton with a capacity of 1.89 liters which is cut out from a cylinder board. The thickness of the material is approximately 0.53 mm. The coating material is applied by using a Steinemann curtain-coating device and it consists of a mixture of a wax and of a copolymer identical to that used in Examples 1 and 2.

The material is placed in an oven at constant temperature with a forced air stream maintained at a temperature of 160°C. The air in the oven is humidified by placing a tub of water in the oven. The temperature of the water is allowed to reach a state of apparent equilibrium. The material remains in the oven for two minutes. Both sides of the material are subsequently coated without reheating it after the application of the coating to its first side. After the application of the coatings, the material is cooled by rapidly immersing it in cold water and then it is dried. The coatings on the material are continuous and devoid of holes and have a glossy and pleasing appearance. When the material is folded both along the folding lines and over the body of the material, it exhibits a better and more acceptable flexibility than the materials which were heated beforehand in nonhumidified air. The board has less tendency to crack and the fibers of the surface of the material have less tendency to tear.

Example 4

The material used in this example is a board for a 0.95 l milk carton which is cut out from a cylinder board. The thickness of the material is 0.4625 mm. The coating material used is the same mixture of a wax and of a copolymer as that used in Examples 1, 2 and 3. The boards are heated beforehand in an oven maintained at a constant temperature of 177°C for 45 seconds. The air in the oven is humidified by placing a tub of water in the oven, as in Example 3. After having coated the first side of the material, the second side is exposed to a row of infrared radiation reheaters for two seconds before coating the second side. After the coating of the second side, the material is cooled by immersing it in cold water and then it is dried. The coatings are continuous and devoid of holes and the second side exhibits a pleasing and glossy coating. When this material is folded both along the folding lines and across its body, it also exhibits better flexibility than the materials heated beforehand in nonhumidified air. The material has less tendency to crack and its surface fibers have less tendency to tear.

Example 5

The material used in this example is a board for a 0.95 l milk carton which is cut out from a cylinder board. The thickness of the material is 0.4625 mm. The coating material used comprises the same

mixture of a wax and of a copolymer as that used in Examples 1, 2, 3 and 4. Before the prior heating, the material is lightly coated with a humectant (diethylene glycol) which has been heated to approximately 93°C in order to guarantee penetration. The cartons are subsequently subjected to a preheating stage as described in Example 3 but without humidification. Both sides of the material are subsequently coated without reheating the material after the application of the coating to the first side. After the application of the coating, the material is cooled by rapidly immersing it in cold water and then it is dried. The coatings of the material are continuous and devoid of holes and exhibit a glossy and pleasing appearance. When the material is folded both along the folding lines and across its body, it exhibits a flexibility comparable to that of a material heated beforehand in humidified air. The material has less tendency to crack and its surface fibers have less tendency to tear.

Example 6

As was indicated above, the positive degassing of the coating composition is an important feature of the invention and it is particularly important in efficiently removing the entrained but undissolved gas from the composition when the latter has to be applied in the form of an essentially continuous adherent film on a flat substrate by using a curtain coating process,

unlike the use of curtain coating processes for the packaging of items.

During comparative trials, a mixture is prepared predominantly comprising a mixture of a paraffin wax with a copolymer of ethylene and of vinyl acetate, with a small amount of a hydrocarbonaceous resin as additive for improving the flexibility of the coating. This composition is used in a Steinemann curtain-coating apparatus to apply thin coatings to a corrugated board. During two different trials, the coating composition is heated to temperatures of 132° and 152°C respectively, before the application. The hot molten mass is circulated in each case for 1 hour before the application of the coating and, during one or other of these trials, use was not made of the degassing apparatus of the "Versator" type described above for removing the entrained gases.

In the case of the composition which is circulated and applied at 132°C, the coating composition exhibits a viscosity of 720 cPs and the composition present in the feed tank for the curtain-coating head is frothy, large bubbles form in the falling curtain and the coatings applied exhibit numerous blisters and other defects.

At 152°C, the bubbles are greatly reduced in the falling curtain but the curtain is less stable because of the lower viscosity of the composition and the

coating is deposited on the substrate with reduced uniformity.

By way of comparison, the same mixture is again applied to the same substrate with the Steinemann curtain-coating device but, in this case, the composition is circulated beforehand through the degassing apparatus of the "Versator" type before applying the coating. The temperature used is 132°C. The curtain formed is essentially devoid of bubbles and stable, and the coating applied to the substrate is uniform and devoid of defects.

Examples 7 to 11 illustrate coating processes used to apply the coatings to various substrates without preheating the substrate. Because of the withdrawal of the preheating, humidification of the substrate is not necessary. In all cases, the "Versator" degassing apparatus is used to remove substantially all the undissolved entrained gas from the hot molten mass coating composition.

Example 7

A laminated substrate comprising an aluminum foil laminated to paper for a bag is coated with a composition in the form of a hot molten mass comprising a mixture of a paraffin wax and of a copolymer of ethylene and of vinyl acetate. The composition exhibits a viscosity of 52 000 cPs at 121°C.

The hot molten mass is heated to a temperature of 188°C and is applied, by means of a Steinemann

curtain-coating apparatus, after degassing, to a moving strip of the aluminum foil laminate which is moved through the falling curtain at a rate of 240 meters per minute. The coating composition is applied to the substrate in an amount of 90 kg per 3 000 m^2. The final appearance of the coating is regarded as being good and is relatively devoid of holes and similar defects.

Example 8

A paper made of nonwoven polyethylene fibers has to be coated with a coating composition in the form of a hot molten mass of the type deriving from mixtures of a paraffin wax and of a copolymer of ethylene and of vinyl acetate. This specific substrate is a heat-sensitive material and thus prior heating thereof should be avoided, if possible.

A coating comprising a predominant a mount of a paraffin wax, exhibiting a melting point of 58°C, mixed with a copolymer of ethylene and of vinyl acetate and a small amount of a hydrocarbonaceous resin, for improving the flexibility and the gloss of the coating, is applied to the described substrate made of nonwoven polyethylene.

After rigorous degassing of the composition with the "Versator" apparatus, the composition is applied to the substrate made of polyethylene with a Steinemann curtain-coating device. The substrate is moved through the falling curtain at a rate of 20 meters per minute. The temperature of the hot molten

mass is 143°C and it exhibits a viscosity of 2 600 centipoises. The coating is applied at a sufficient thickness to obtain 94.57 kg of coating composition per 3 000 m^2 of substrate. The barrier properties preventing the transmission of the coated substrate moisture, as determined by the test according to the TAPPI standard F448m-49 (entitled Degree of transmission of water vapor), expressed in grams of water transmitted through the coated substrate over an area of 645 cm^2 for 24 hours and in an atmosphere having a relative humidity of 95% and at a temperature of 38°C, are very weak. The transmission of vapor through the flat substrate as a function of this measurement unit is 0.57 and, through the folded substrate, it is 0.85.

Example 9

A corrugated board of the type used to manufacture boxes for transporting frozen poultry is coated with a composition formed of a wax and of a copolymer of the general type described above. The coating composition is heated to a temperature of 135°C (viscosity of 500 cPs) and a series of blanks used to form poultry boxes is moved on conveyor belts through the falling curtain at a rate of 150 m per minute. The thickness of the coating applied to the blanks made of corrugated board corresponds to 27 kg per 1 000 m^2. The coatings are smooth, uniform in appearance and relatively devoid of holes and other visible defects.

Example 10

A strip of regenerated cellulose, known and sold under the name of "Cellophane", moved at a rate of 82.5 m per minute, is coated, using a Steinemann curtain-coating device, with a composition in the form of a hot molten mass comprising:

30% by weight of a copolymer of ethylene and of vinyl acetate comprising from 20 to 30% by weight approximately of vinyl acetate and having a melt index of 10 to 20 approximately,

70% by weight of paraffin wax (melting point of 52 to 53°C).

The composition is applied in the form of a hot molten mass to the "Cellophane" substrate at a temperature of 124°C (viscosity of 1 280 cPs) at a rate which makes possible the application of 172.48 kg of the composition over 3 000 m^2 of substrate. The coating applied to the "Cellophane" in this way is devoid of defects and exhibits a glossy appearance.

Example 11

A bleached board weighing 94 kg, of the type used to manufacture [illegible] cups for comprising a soft white cheese, [illegible] cream, sandwich ingredients, and the like, is progressed through a falling curtain in the form of a strip at a rate of 147 meters per minute. The coating composition used is the same as that which was used in the above Example 8. The temperature of the coating composition is 149°C and the

composition is distributed over the surface of the substrate according to an amount equivalent to 85.59 kg per 3 000 m^2. Suitable coatings are obtained on this relatively thick material without using preheating.

Example 12

Opaque crystal paper weighing 13.6 kg, which has been printed and glazed on one side by the manufacturer, is subjected to coating on the opposite side by the process of the present invention. The coating composition comprises a mixture of a wax and of a copolymer applied with a Steinemann curtain-coating machine to a strip of the substrate moving at a rate of 330 meters per minute. The composition exhibits a viscosity of 8 000 cPs at 121°C and is applied at a temperature of 163°C without preheating the substrate. The composition is applied with a thickness equivalent to 43.12 kg of the composition per 3 000 m^2 of the paper.

The coating obtained on the crystal paper under these conditions is smooth and devoid of bubbles, holes and blisters. The degree of transmission of water vapor, as defined above, is 0.21 in the case of the flat substrate and 0.23 in the case of the folded substrate.

In addition to substrates of the type described in the above examples, excellent coatings have been obtained, by using hot and viscous molten masses of the type described above comprising mixtures of a paraffin

and/or microcrystalline wax with copolymers of ethylene and of vinyl acetate, on other substrates, such as plywood, sulfite paper, by adding clay to the coating in order to render the paper opaque, 6 point bristol board and various other substrate materials. In general, the Applicant Company has found that the degassing process disclosed in the present application and constituting a noteworthy feature of the present invention is particularly important and advantageous when the viscosity of the coating material is at least 300 centipoises at a temperature ranging up to 149°C. With viscous coatings of this type, it is important to subject the coating composition to the vacuum rectification technique described in order to remove the entrained gas.

It can be seen from the detailed description and examples given above that the process of the present invention can be most advantageously used for coating both sides of a sheet of a relatively porous material with various compositions in the form of hot molten masses in order to form a continuously adherent coating. However, not all the information given above is necessarily restricted to such applications. For example, to date, it has been very difficult to satisfactorily obtain adherent coatings of a composition formed of a wax and of a copolymer of the type described on various substrates having a relatively smooth and substantially nonporous surface.

These substrates comprise, for example, various metals, numerous plastics (thermoplastics or thermosetting plastics), hard rubber, smooth and dense papers, such as crystal paper, and the like. The Applicant Company has now found that, if nonporous substrates are appropriately heated beforehand and then curtain coated while maintaining them in the heated state, the mixtures of waxes and of copolymers thus applied adhere to the surface of the substrate with a greatly improved tenacity.

From the above description of the present invention, it is seen that the process provided offers certain advantages and certain improvements with respect to the coating processes which have been used to date, in particular the processes used to apply a substantially continuous adherent coating which is devoid of defects to the surface or surfaces of the fibrous material of the type described, the coating being applied substantially parallel to the surface. The apparatus used is simple and economic in construction and is characterized by a long service life without disadvantages.

As mentioned above, the different variables which have to be taken into account in the precise determination of the temperature to which a specific material can or has to be heated beforehand and of the degree of humidification which is desirable render a

precise definition of these parameters impossible in the general description of the invention.

The invention is naturally not limited to the embodiments described and represented and is capable of taking various alternative forms coming within the scope and the spirit of the invention.

SUMMARY

A. Process for coating a surface of a sheet of material with a composition in the form of a hot molten mass, characterized by the following points, separately or in combinations:

1. It consists in melting the composition in the form of a hot molten mass, in removing substantially all the entrained and undissolved + gases from the molten composition and in depositing, on the surface of the sheet of material, substantially parallel to said surface and in substantially continuous contact with it, a coating in the form of a membrane of the molten composition in the form of a degassed hot molten mass.

2. The removal of the undissolved entrained gases is carried out by spreading the composition in the form of a hot molten mass in an agitated thin layer and by simultaneously subjecting the agitated thin layer to a vacuum rectification.

3. The sheet of material is heated before depositing, on the sheet, the composition in the form of a degassed hot molten mass.

4. The composition in the form of a hot molten mass exhibits a viscosity of at least 300 cPs at a temperature ranging up to 149°C.

5. The sheet of material is nonporous.

6. The sheet of material is a porous material exhibiting porosity characteristics similar to those of paper.

7. The composition in the form of a molten mass comprises a mixture of 80 to 30 parts of an oil-derived wax, chosen from a paraffin wax, a microcrystalline wax and mixtures of these, and correspondingly of 20 to 70 parts of a copolymer of ethylene and of vinyl acetate exhibiting a vinyl acetate content of between 10 and 40% by weight and a melt index of 3 to 300 approximately.

8. Said process consists in melting the composition in the form of a hot molten mass, in substantially degassing said molten composition, in heating the sheet of material and in depositing, almost immediately, on the surface of this sheet of material, a coating in the form of a membrane of the composition in the form of a substantially degassed hot molten mass.

9. The sheet of material is nonporous.

10. In order to coat both surfaces of a sheet of material with a composition in the form of a hot molten mass, said process consists in melting the composition in the form of a hot molten mass, in

substantially degassing the molten composition, in depositing, on a surface of the sheet, a coating in the form of a membrane of the substantially degassed molten composition, in heating the coated sheet and in subsequently coating the uncoated side of the sheet in the same way as the first side.

11. The heated sheet is passed through a falling curtain of the composition in the form of a substantially degassed molten mass.

12. The copolymer of ethylene and of vinyl acetate exhibits a vinyl acetate content of between 10 and 20% by weight.

13. The heating is carried out in a humidified atmosphere.

14. The coating formed on the second side of the sheet is in the form of a continuously adherent film.

15. The sheet of material is a substrate made of paper.

B. Apparatus for applying a coating of a composition in the form of a hot molten mass to a sheet of fibrous material, for example paper or similar material, characterized by the following points, separately or in combinations:

1. It comprises a heating device for heating the composition in the form of a hot molten mass, a means for forming a falling molten curtain of said composition, a receiving container positioned below the

curtain-forming means, for receiving the liquid falling from the curtain, a pipe connected between the curtain-forming means and the liquid receiving container, in order to distribute the liquid from the container to the curtain-forming means, a degassing means in the pipe for degassing the liquid before its entry into the curtain-forming means, and a conveying device extending towards and beyond the falling curtain formed by the curtain-forming means, in order to move the sheet of material through the falling curtain.

2. The degassing means comprises a means for spreading the liquid in the form of an agitated thin film and a means for vacuum rectifying the agitated thin film in order to remove therefrom the undissolved entrained gases.

3. The means for spreading the liquid in the form of an agitated thin film comprises a rapidly rotating centrifuge bowl exhibiting a lower surface and a means for distributing the liquid over the lower surface of the centrifuge bowl.

4. The means intended to vacuum rectify the agitated thin film comprises a closed chamber surrounding the centrifuge bowl and a means for placing the chamber under vacuum.

Approved

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Brussels, 26 September 1967

p.p. : Company known as:

CONTINENTAL OIL COMPANY

[illegible signature]

5 + "dissolved" change to "undissolved"

Company known as: CONTINENTAL OIL COMPANY

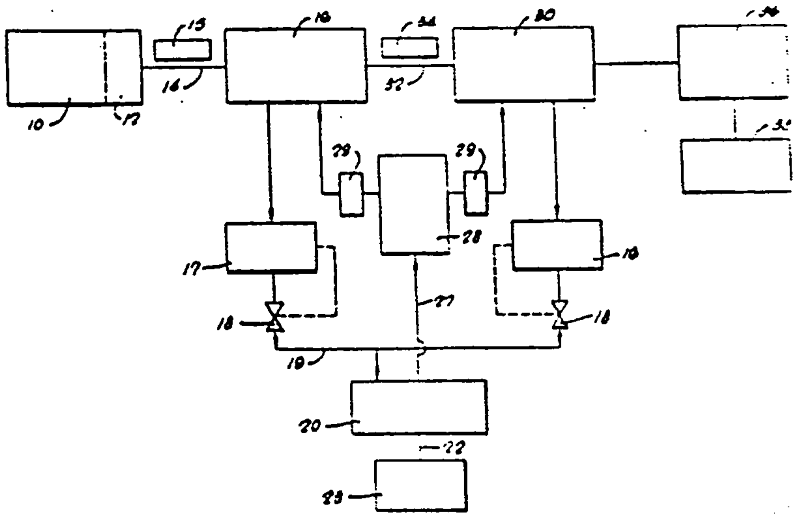

Fig-1

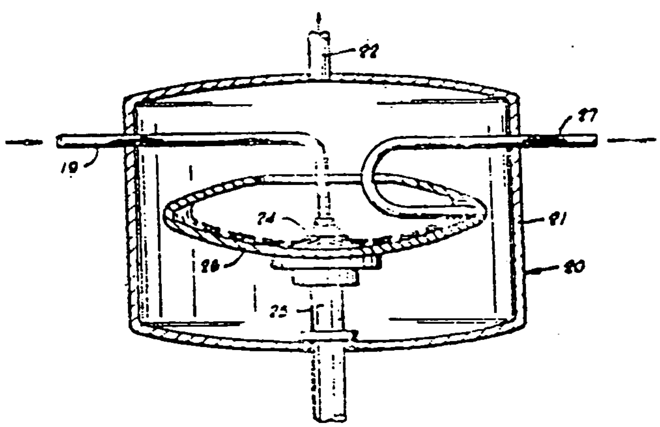

Fig-2

Brussels, 26 September 1967

p.p. : Company known as: CONTINENTAL OIL COMPANY

[illegible signature]

Translator's Report/Comments

Y ur ref: KILLWORTH-61417 **Your order of (date):** 9/11/2000

In translating the above text we have noted the following apparent errors/unclear passages which we have corrected or amended:

Page/line*	Comment
General comment	A number of words in this document were illegible because of the poor quality of the copy.
3/-5	"en un" → "un"
8/18	"un cas" → "cas"
10/11	"ces" - might be "ses".
13/-7	The word between "anneau" and "disque" looks like "ou".
15/19	The word after "matière" looks like "ou".
16/15	"ses" - might be "ces".
19/-4 et seq.	"cps" → "cPs"
21/18	"met" → "omet"
21/19	"carton" → "boîte"
21/-8	"autres" → "d'autres"
23/2	"soit" → "soient"
26/6	"à la distinction de" - appears to mean "unlike" and so translated.
28/12	First word could also be "ou" but "et" preferred.
29/2	The "F" could be "P".

* This identification refers to the source text. Please note that the first paragraph is taken to be, where relevant, the end portion of a paragraph starting on the preceding page. Where the paragraph is stated, the line number relates to the particular paragraph. Where no paragraph is stated, the line number refers to the page margin line number.

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Your ref: KILLWORTH-61417 **Your order of (date):** 9/11/2000

In translating the above text we have noted the following apparent errors/unclear passages which we have corrected or amended:

Page/line*	Comment
29/16	There is something illegible after "cps".
32/-7	"au procédé" → "aux procédés"
34/25	"celle-ci" → "celles-ci"

* This identification refers to the source text. Pl ase note that the first paragraph is taken to be, where relevant, the end portion of a paragraph starting on the preceding page. Where th paragraph is stated, the line number relates to the particular paragraph. Where no paragraph is stated, the line number refers to the page margin line number.

TRC1 1.7.92